X-ray Characterization of Cement-based Materials: Previous Applications & New Opportunities

Kimberly Kurtis
School of Civil and Environmental Engineering
Georgia Institute of Technology
Atlanta, Georgia

Collaborators:
CXRO at ALS: G. Denbeaux, A. Lucero
UC Berkeley: P.J.M. Monteiro
Georgia Tech: A.P. Wilkinson, A.C. Jupe, N.N. Naik
APS: P. Lee
NIST: P. Stutzman
IBNAM at Northwestern Univ.: S.R. Stock

August 31, 2004

Georgia Tech College of Engineering

School of Civil & Environmental Engineering

What are cement-based materials?

Any material that uses a mineral cement as a binder

Classes of mineral cement: portland (calcium silicate-based) and calcium aluminate, some dental and bone cements

Cement paste =  + 

Mortar =  +  + 

Concrete =  +  +  + 

Why research cement-based materials?

Concrete is the most widely used building material, with more than 12 billion tons of placed annually.

Annual Regional Cement Consumption, million tons

	1994	2000	2005
Europe*	313	393	432
Asia	680	853	1000
Middle East	65	79	82
Africa	63	71	77
North America	90	92	92
South&Central America	92	118	142
Misc.	7	9	10
Total	1310	1625	1835

* *World Cement*, V27(5).

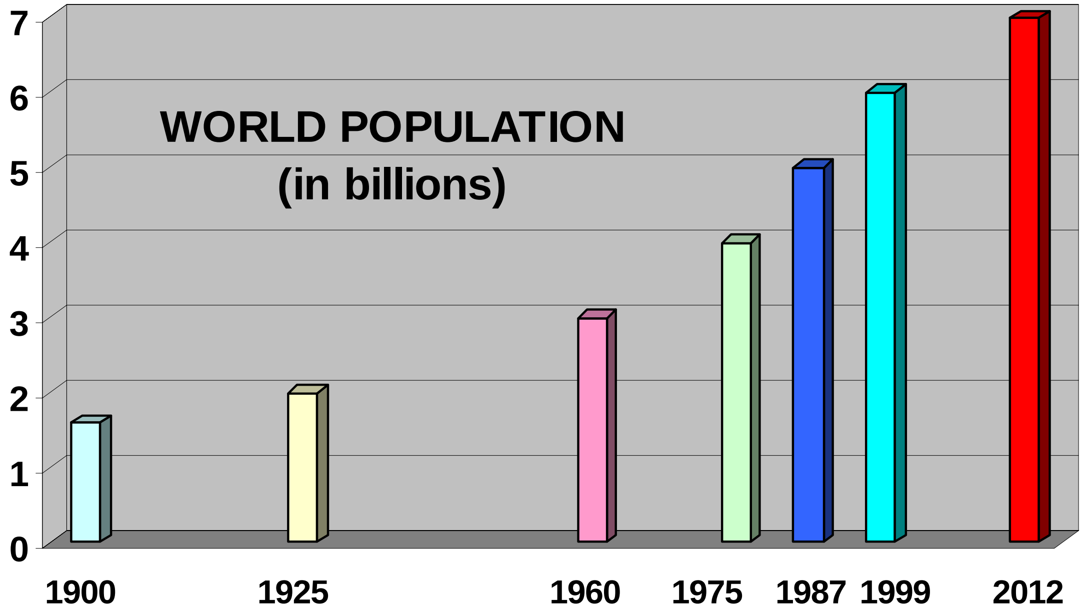
Why research cement-based materials?

Increasing infrastructure demands

- increasing population
- construction in more aggressive environments
- increasing performance expectations

Environmental concerns

- energy consumption
- CO_2 production
- durability



Why research cement-based materials?

Despite the widespread use of cement-based materials, fundamental understanding is lacking with regard to:

- chemistry and structure during manufacture
- hydration chemistry
- nano and microstructure of cement-based materials
- behavior under load (fracture and creep) and during shrinkage
- structure-property relationships
- durability
- effect of combinations of loading and environmental exposure

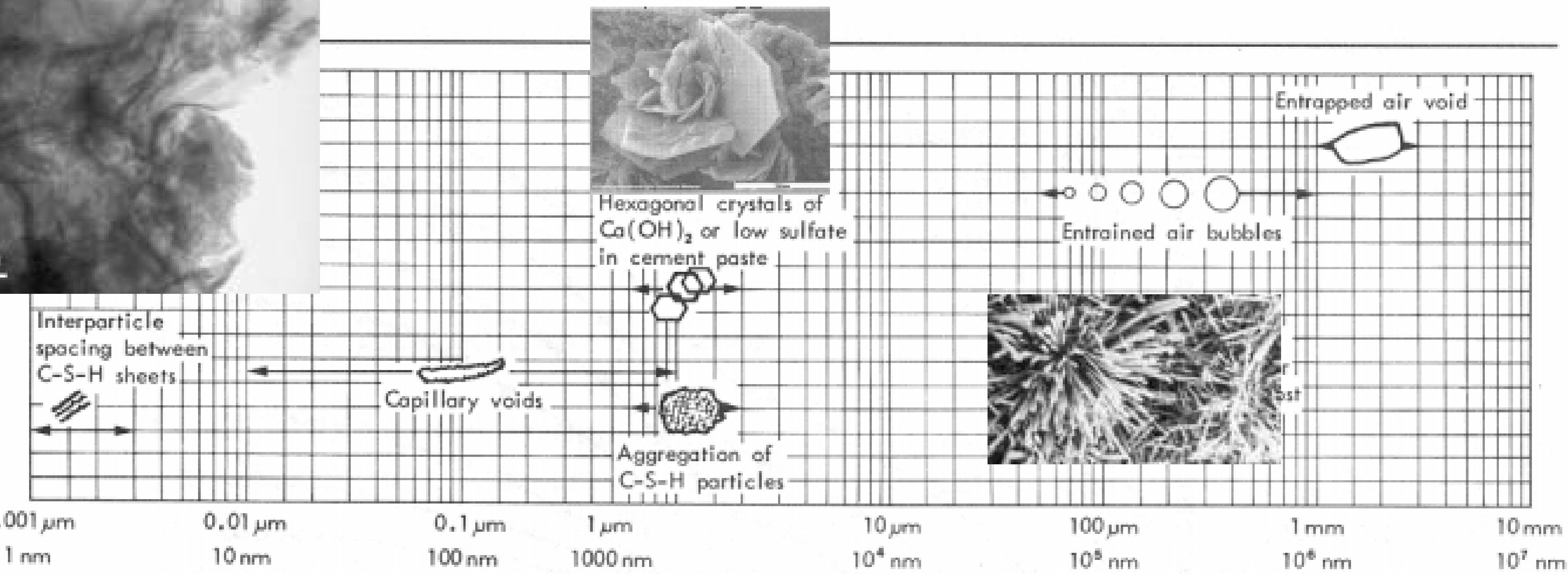
These gaps limit our ability to reliably produce cement-based materials with specialized physical and mechanical properties and that exhibit long-term durability.

Challenges Associated with Characterization of Cement-based Materials

- Hydrated systems that change with removal of water
- Optically opaque materials, but sub-surface or volumetric characterization is often desirable
- Complex materials that are heterogeneous on multiple scales (nano $\rightarrow$ micro $\rightarrow$ meso $\rightarrow$ macro)
- Want to resolve the smallest features of the structure, while still capturing the different spatial structures that comprise the whole
- Effect of time can be important $\rightarrow$ fast imaging
- Non-destructive characterization is desirable

Structure of cement-based materials

- Concrete is heterogeneous on multiple scales



1-5 nm
Ult. strength
Adsorption

<50nm
Shrinkage
Creep
Durability

Applications of X-ray Imaging

- Cement production
- Cement hydration
- Behavior under loading
- Degradation/durability

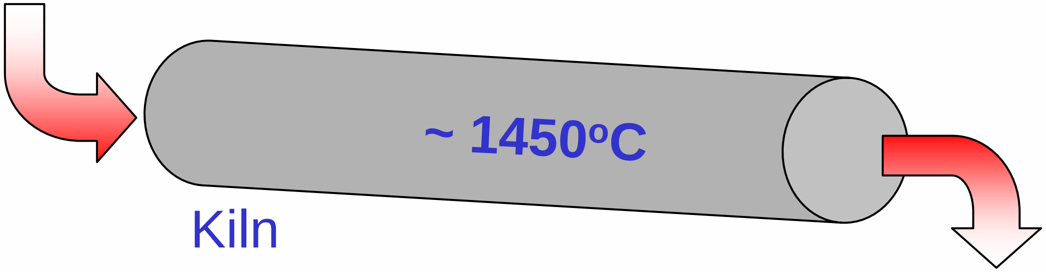
Cement Production

$CaCO_3$ (limestone)

$2SiO_2 \bullet Al_2O_3$ (clay, shale)

Fe_2O_3 (iron oxide)

SiO_2 (silica sand)



$CaO \bullet SO_3 \bullet 2H_2O$

Gypsum + Clinker

$3CaO \bullet SiO_2$

$2CaO \bullet SiO_2$

$3CaO \bullet Al_2O_3$

$4CaO \bullet Al_2O_3 \bullet Fe_2O_3$

Finished cement ← interground

Cement Production

Studies to date in this area have almost exclusively relied upon synchrotron powder diffraction, rather than imaging.

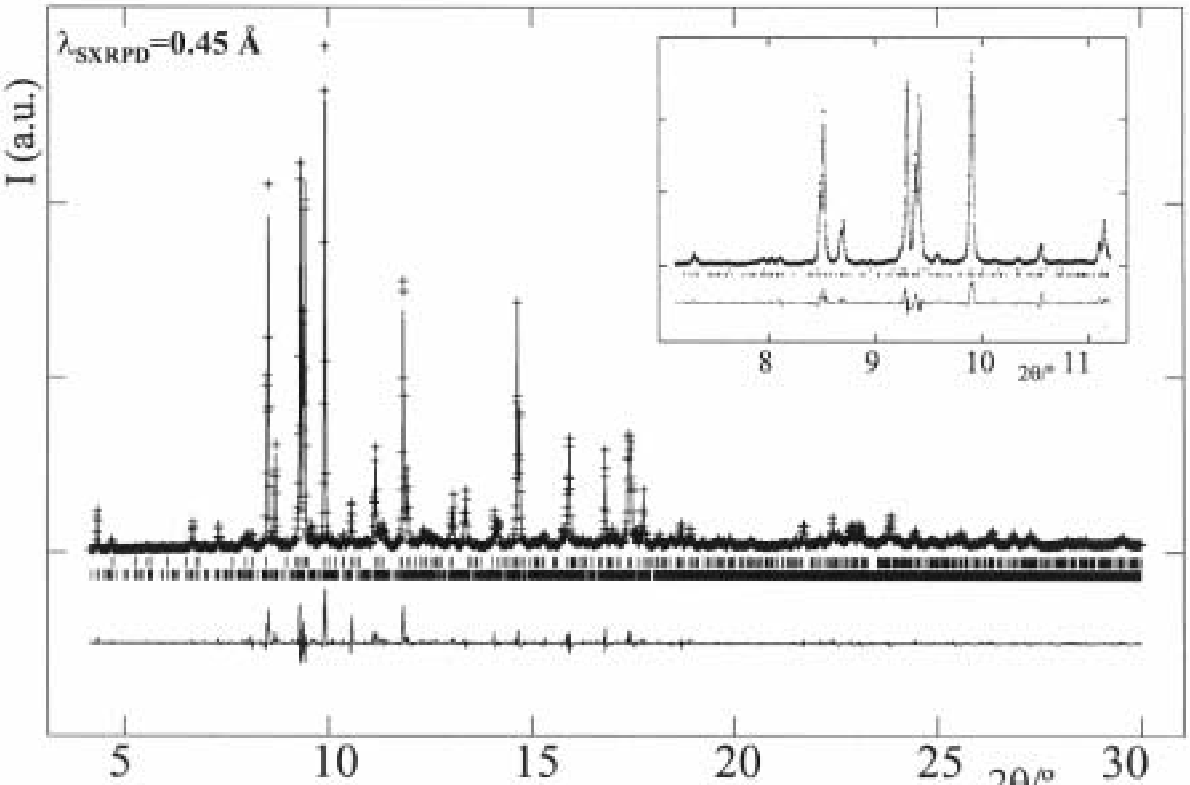


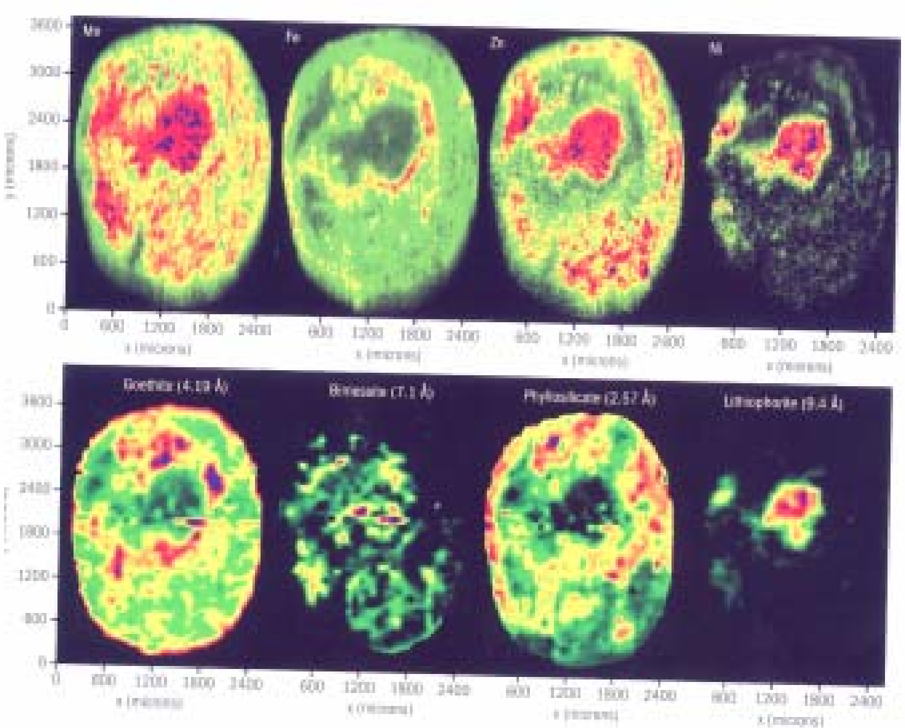
Fig. 1. SXRPD Rietveld plot for C_3S. The inset shows the fit to the most representative region for C_3S.

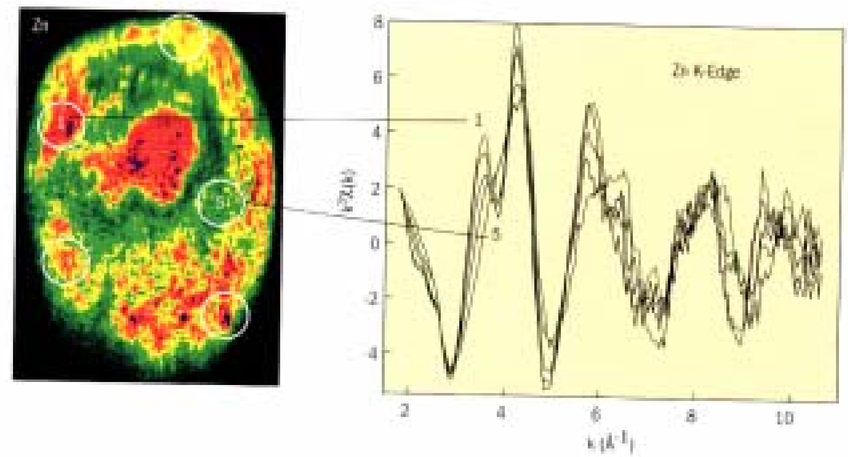
De La Torre, Bruque, Campo, and Aranda, *Cement and Concrete Research*, 32:1347-56 2002.

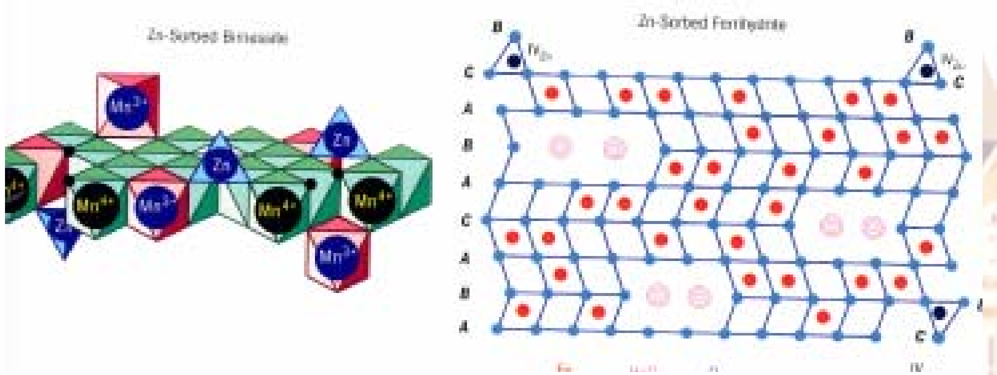
Cement Production: Would Imaging be Useful?

An anologue in geochemistry: combined μSXRF- μSXRD for elemental mapping on a soil nodule.

Combined with μEXAFS to examine Zn sequestration.







Manceau, Tamura, Marcus, MacDowell, Celestre, Sublett, Padmore, and Sposito, *ALS Activity Report,* 2002.

Cement Production

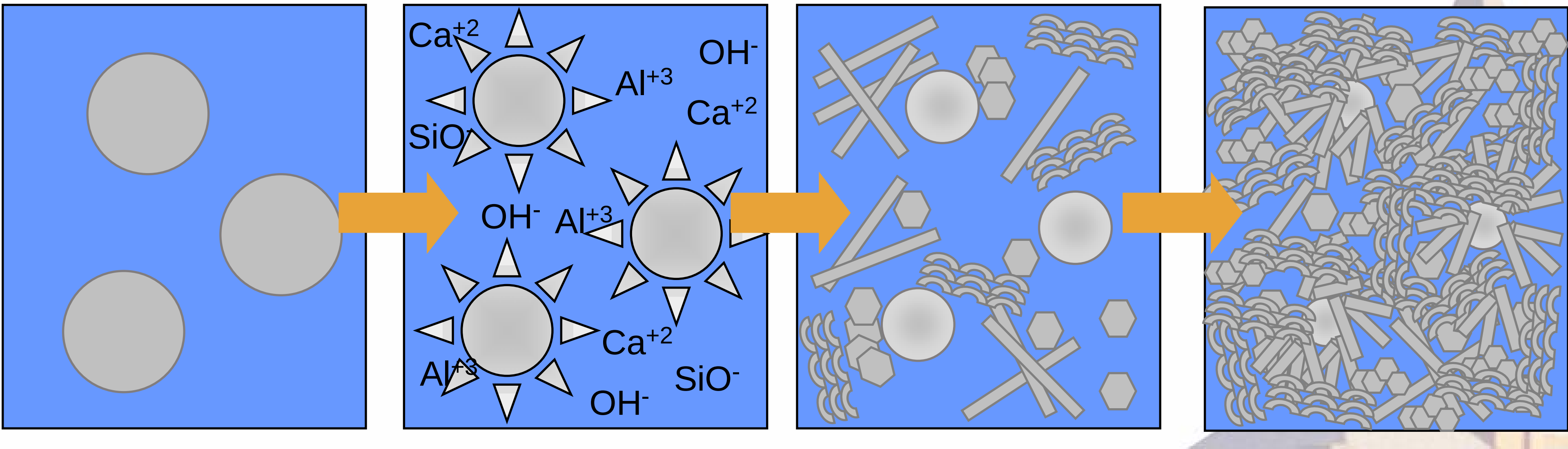
Research opportunities exist in:

- Identification of phases existing in unhydrated cement and clinker
- Quantification of those phases
- Characterization of phase structure as influenced by the introduction of hazardous and non-hazardous (introduced for improved production or hydration) impurities
- *In situ* characterization at high temperature (to 1500 C)

Cement Hydration

When water is added to cement, what happens?

- Dissolution of cement grains
- Growing ionic concentration in “water” (now a solution)
- Formation of compounds in solution
- After reaching a saturation concentration, compounds precipitate out as solids (“hydration products”)
- In later stages, products form on or very near the surface of the anhydrous cement



Cement Hydration

Very generally, portland cement hydration proceeds by:

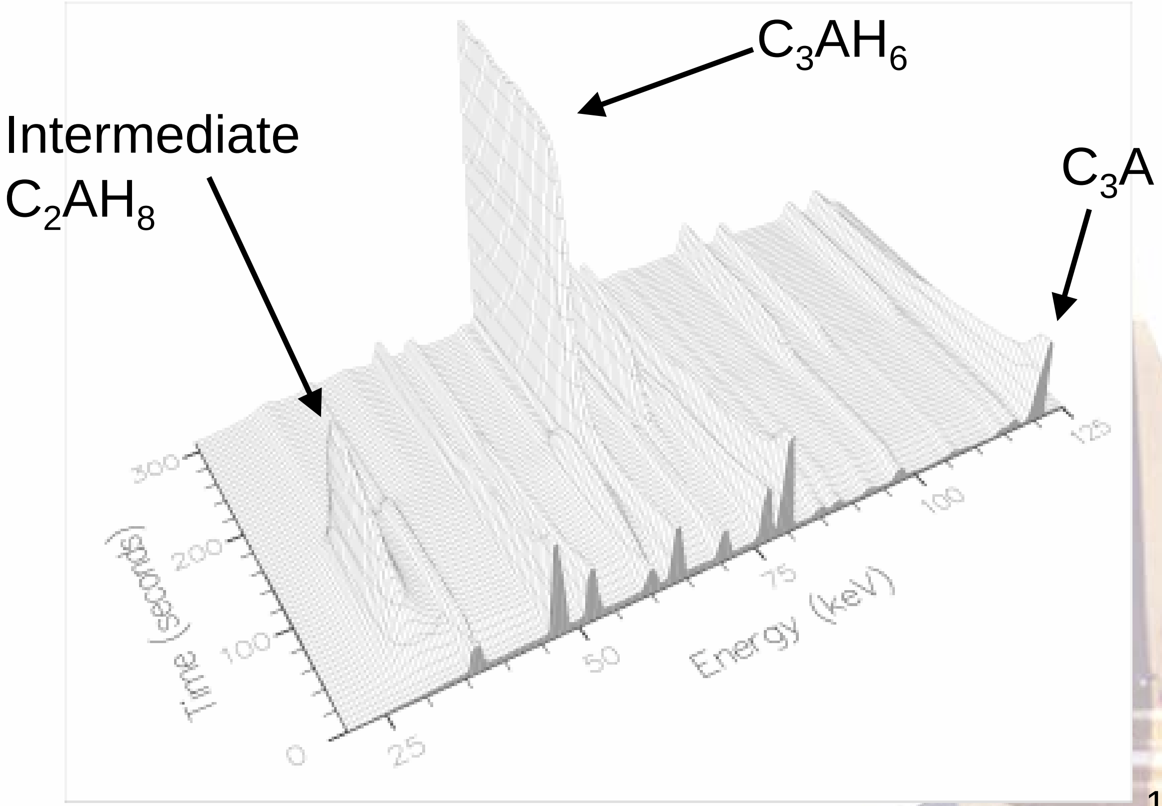
$$\left.\begin{array}{l} 3CaO\bullet SiO_2 \\ 2CaO\bullet SiO_2 \end{array}\right. \longrightarrow \text{C-S-H} + Ca(OH)_2$$

$$\left.\begin{array}{l} 3CaO\bullet Al_2O_3 \\ 4CaO\bullet Al_2O_3\bullet Fe_2O_3 \end{array}\right. \longrightarrow \text{Ettringite + Monosulfate Hydrate}$$

Cement Hydration: EDXRD

- Rapid data acquisition allows for in situ monitoring of cement hydration in real time

An intermediate in the hydration of C_3A (or $3CaO{\bullet}Al_2O_3$) was definitively identified using time-resolved EDXRD at Daresbury SRS.



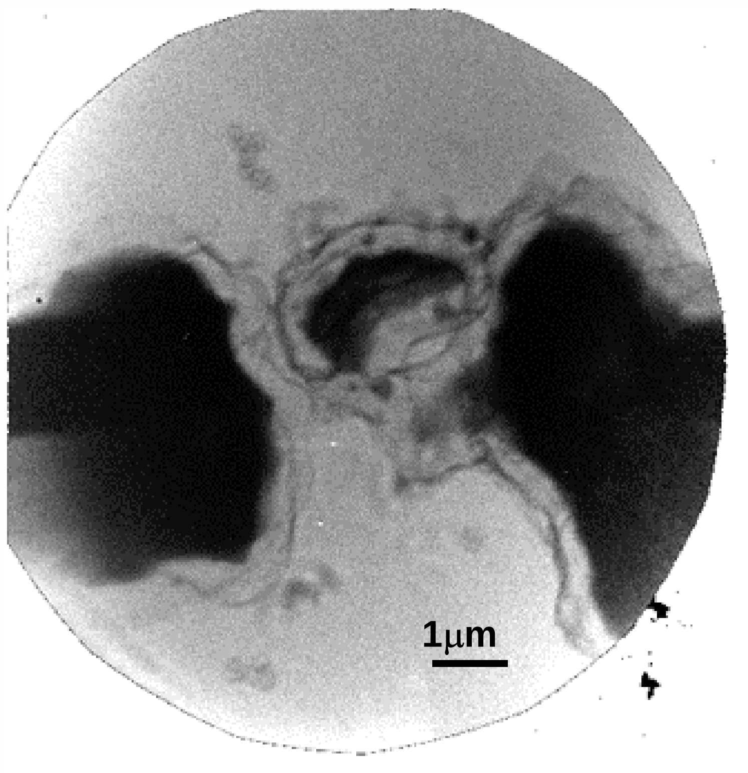
Jupe et al., Phys. Rev. B53, R14697 (1996)

XM-1: Beamline 6.1.1 at ALS

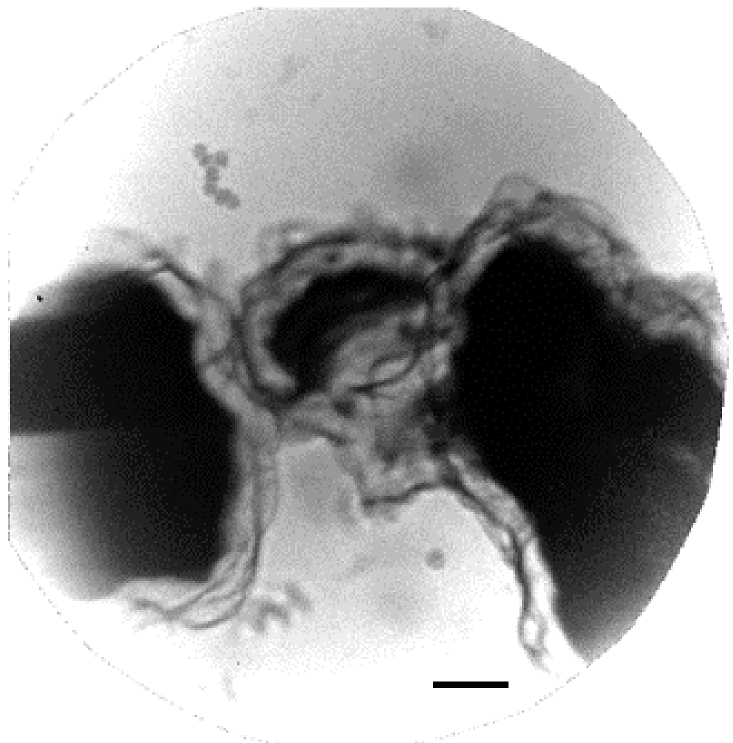
XM-1 is operated and maintained by the Center for X-ray Optics (CXRO)

Cement Hydration: TXRM

Examination of hydration of calcium sulfoaluminate cements (Kleinite $C_4A_3\overline{S}$ or $4CaO\cdot 3Al_2O_3\cdot SO_4$)



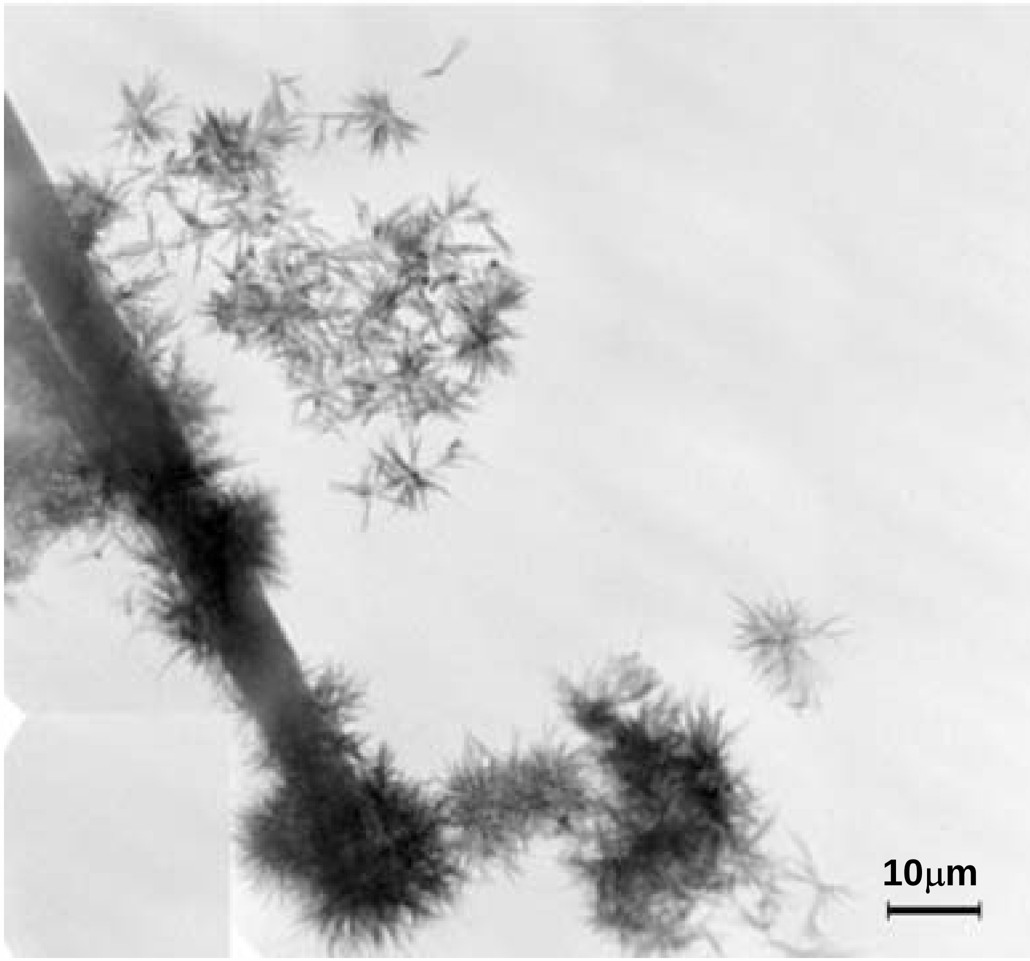
30 min.



85 min.

2400x; λ=2.4nm

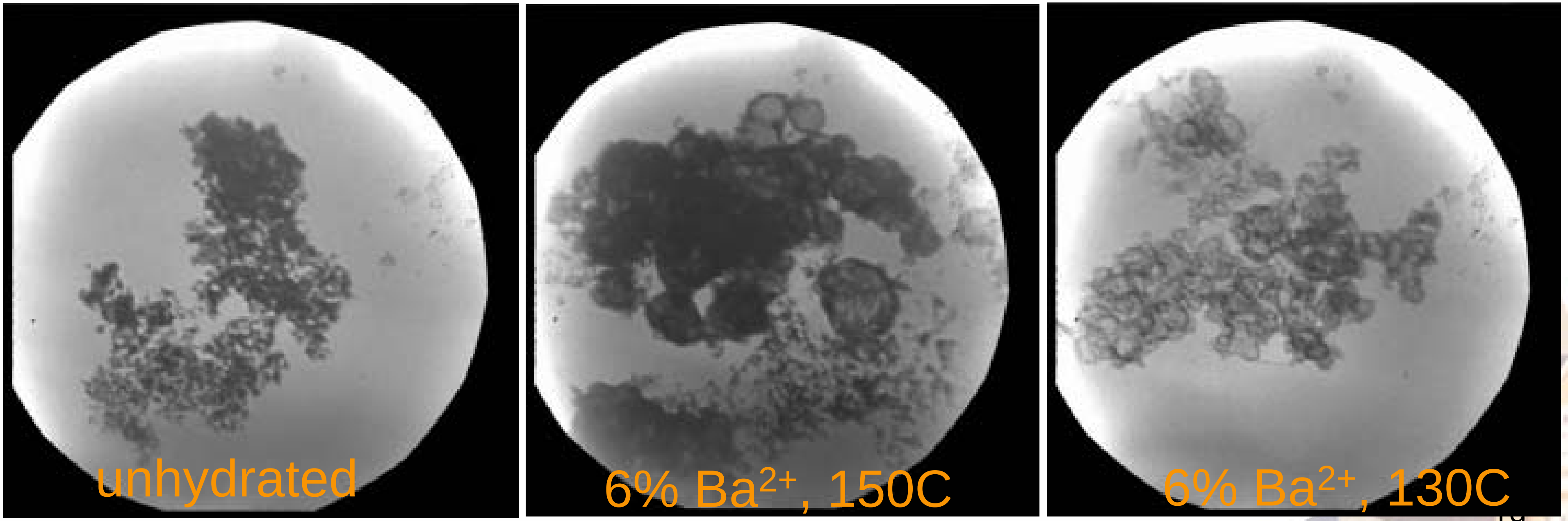
Cement Hydration: TXRM



Tiles composed from X-ray images of mixture of 30.0% $C_4A_3\bar{S}$ + 53.4% $C\bar{S}$+ 16.5% C (by mass) after 4.5 hours in saturated calcium hydroxide + 0.1 M $CaCl_2$ solution, w/s=10

Cement Hydration: TXRM

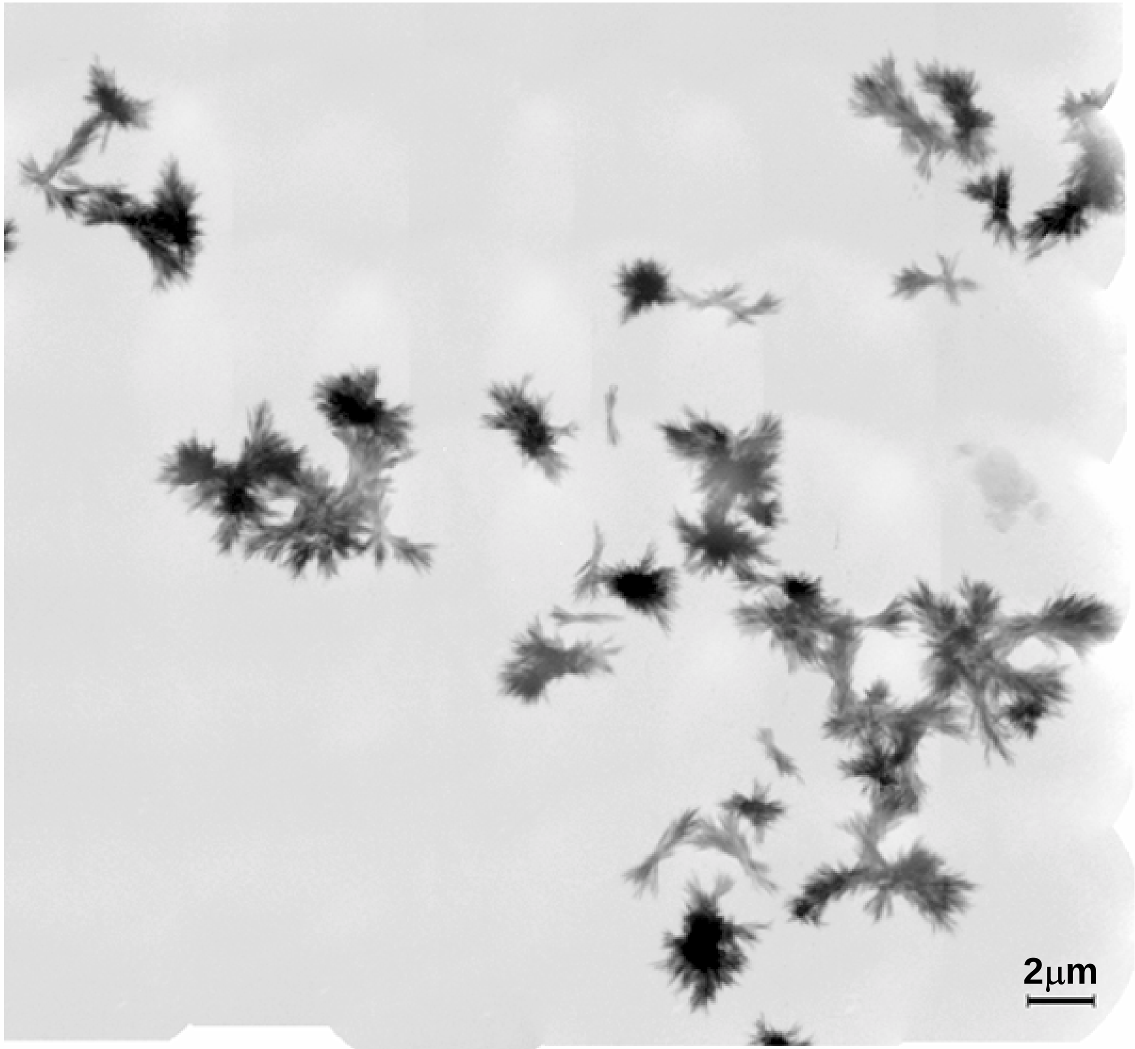
- Investigation of thermal treatment on hydration of low-energy, β-$2CaO \cdot SiO_2$ rice hull ash cements.
- RHA cements processed at higher temperatures (150°C vs. 130°C) reacted more rapidly, with products visible through TXRM at earlier ages and with greater abundance.



2400x; λ=2.4nm

K.E. Kurtis and F.A. Rodrigues, *Cement and Concrete Research*, April 2003, V.33(4):509-515.

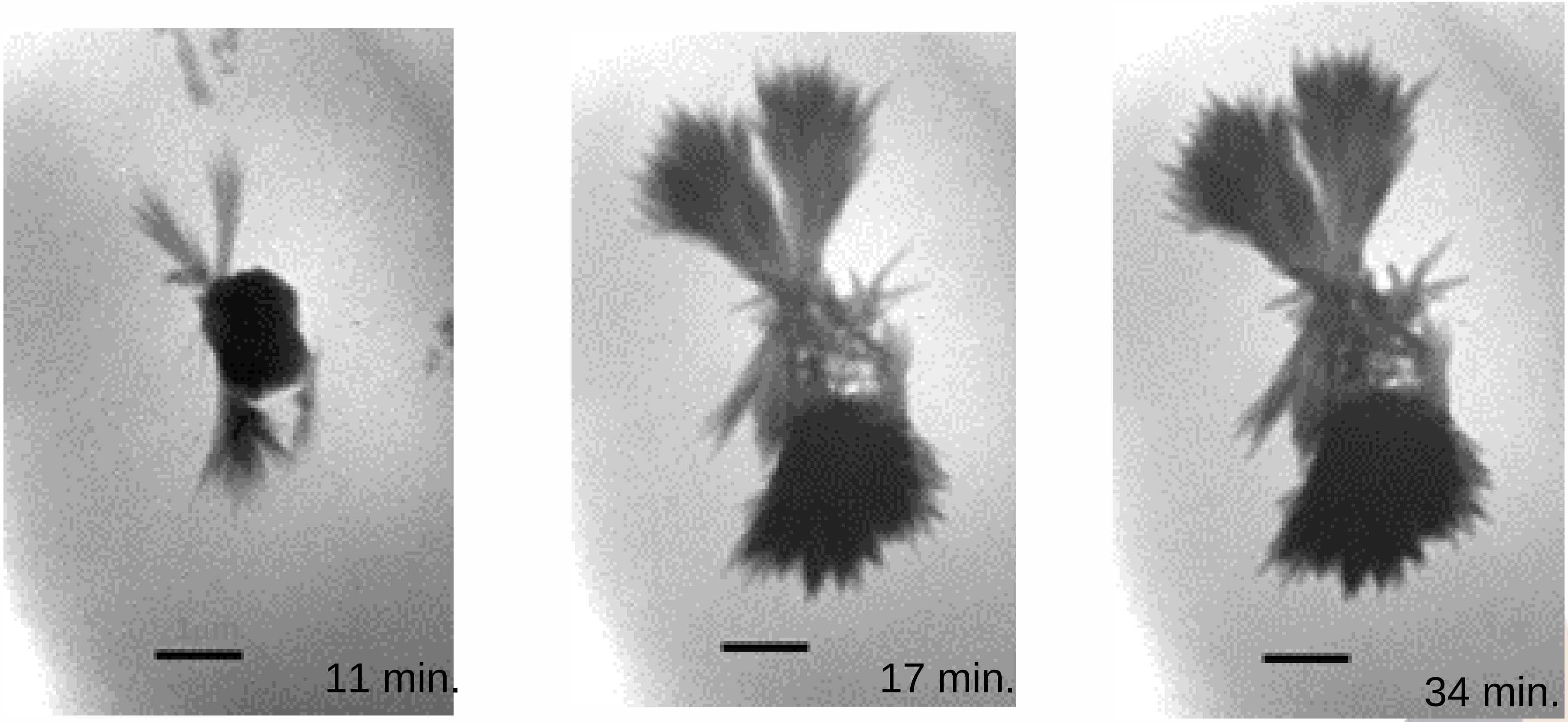
Pozzolanic Reaction: TXRM



Tiled x-ray images of chemical grade silica gel after 2 hours in saturated $Ca(OH)_2$ solution.

- Reaction of finely divided silicates in alkaline calcium-rich solutions generally resulted in products with dendritic microstructure
- The ‘sheaf of wheat’ morphology was particularly prevalent

Pozzolanic Reaction: TXRM



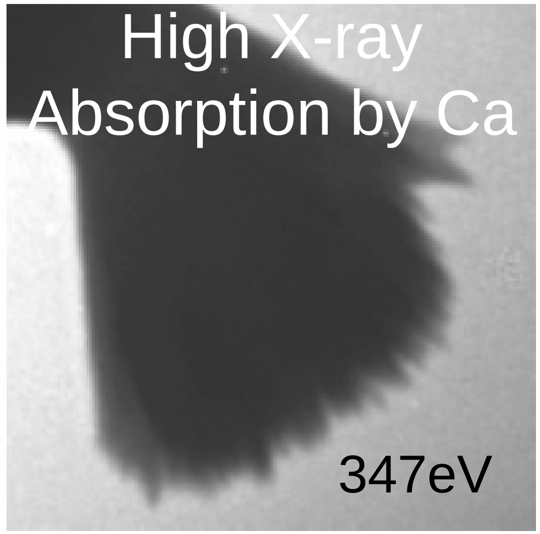
Reaction of silica gel in 0.7M NaOH + 0.1M $CaCl_2$ solution over time results in development of “sheaf of wheat” microstructure.

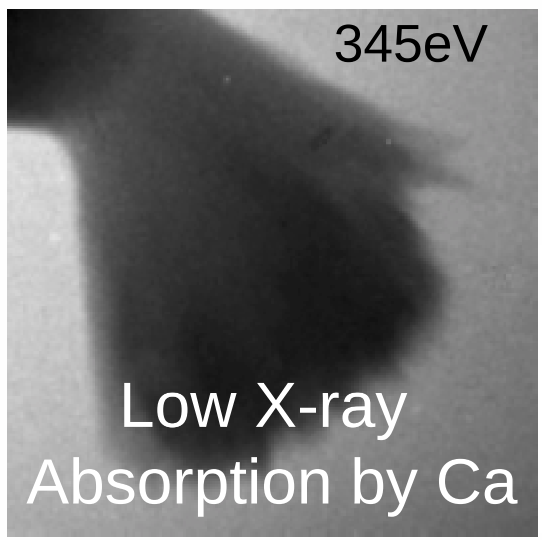
2400x; λ=2.4nm

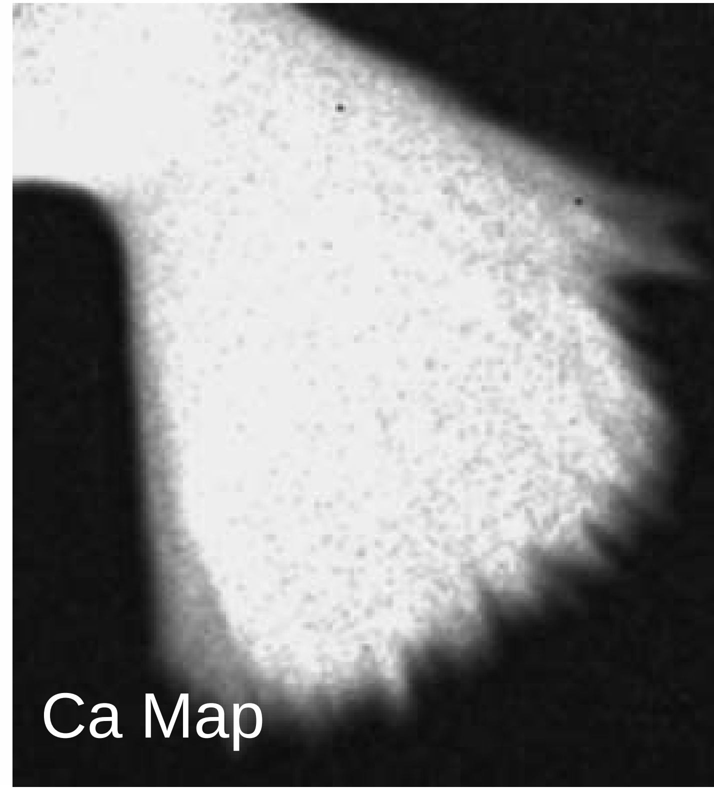
K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, and W. Meyer-Ilse, *Journal of Microscopy*, December 1999, V196: 288-298.

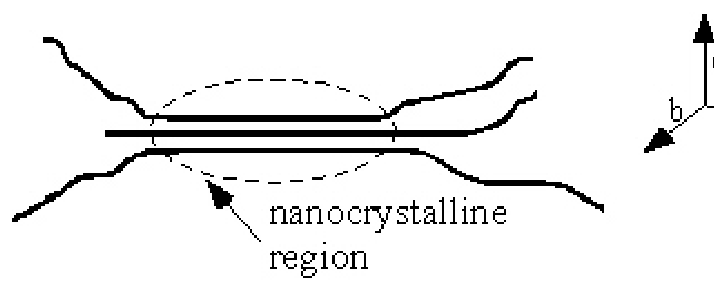
E. Gartner, K.E. Kurtis, and P.J.M. Monteiro, *Cement and Concrete Research*, May 2000, V30 (5):817-822.

Pozzolanic Reaction: Ca-edge Spectromicroscopy using TXRM









E. Gartner, K.E. Kurtis, and P.J.M. Monteiro, *Cement and Concrete Research*, May 2000, V30 (5):817-822.

Transmission Soft X-ray Microscopy at XM-1

<u>Advantages</u>

- Designed for ease of user operation
- Samples can be studied wet
- No artifacts from drying or pressure change
- Able to observe and record ongoing reactions
- High resolution (43 nm)
- Characterization of internal structure
- Identify areas of elemental concentrations

<u>Limitations</u>

- Small sample size – nearly 2D imaging
- High solution-to-solid ratio needed for transmission
- Limited spectromicroscopy capabilities
- Limited availability

Cement Hydration: Synchrotron Microtomography

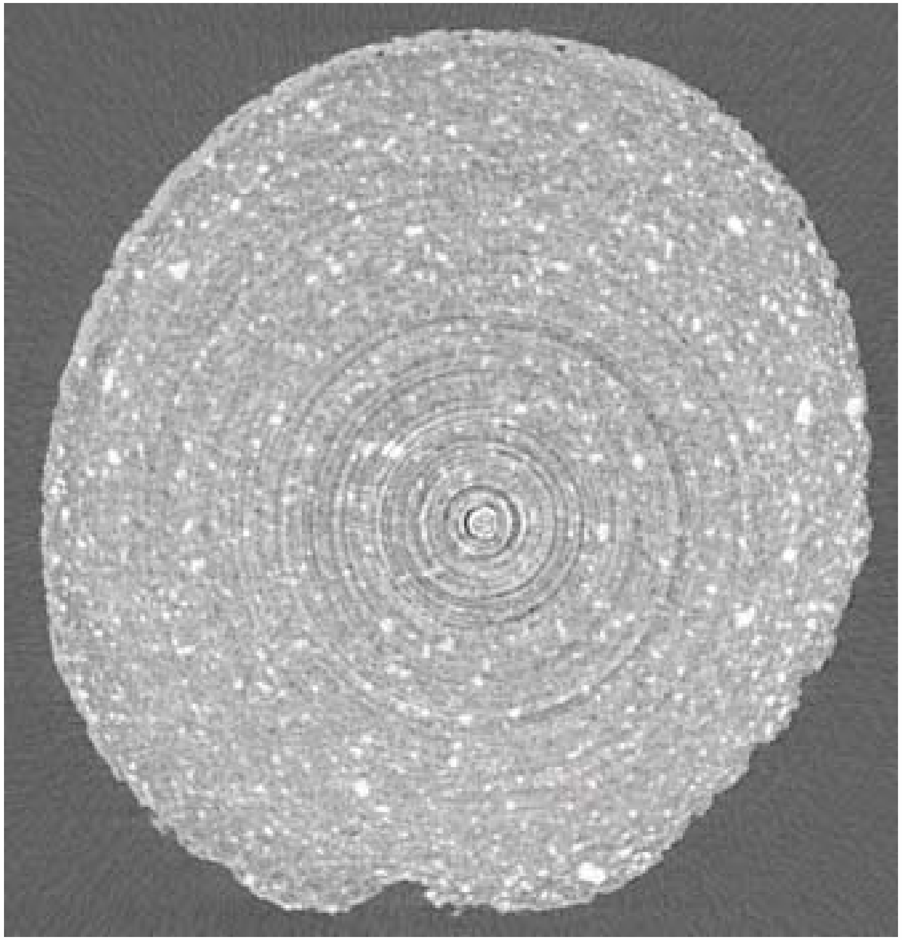
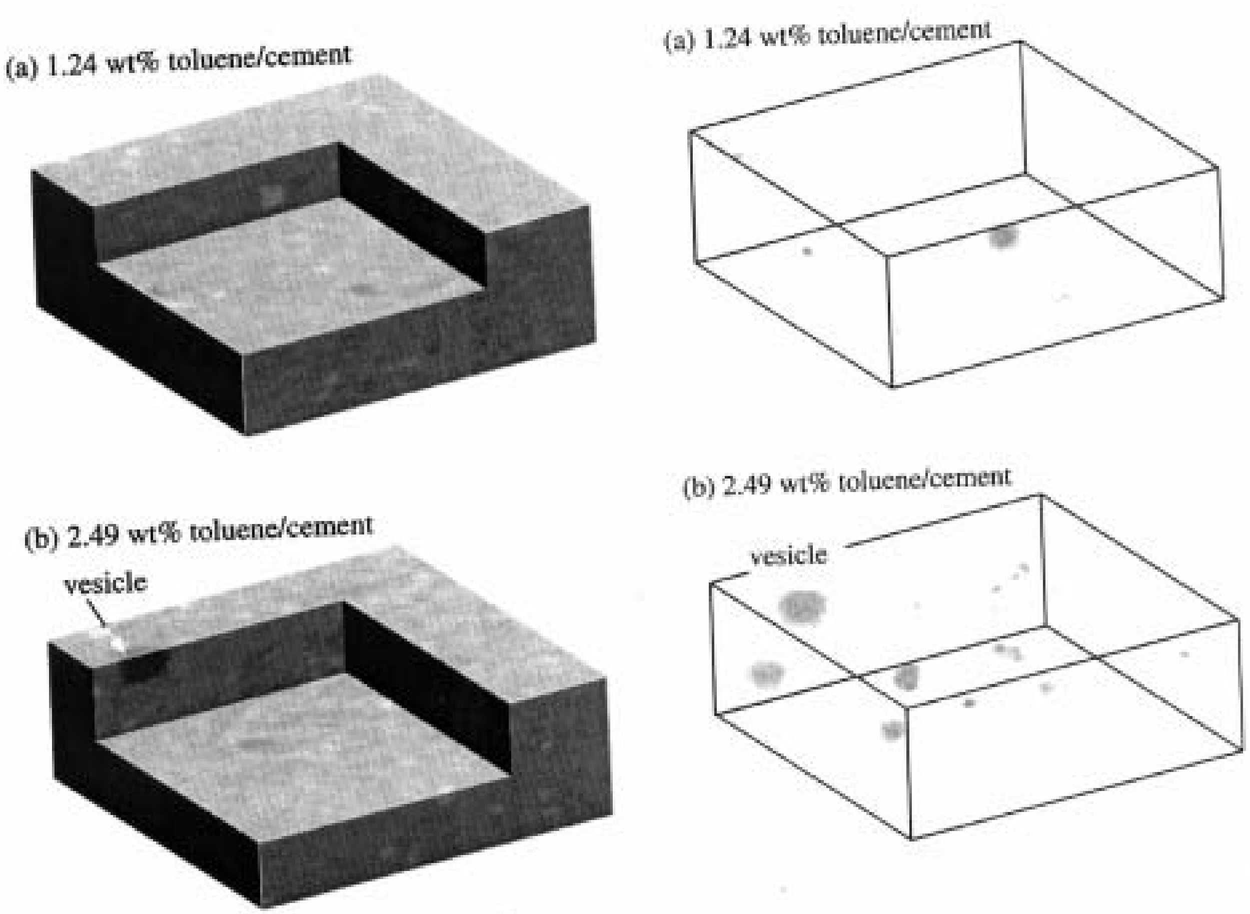


Image: S.R. Stock, Northwestern Univ.

- 5 μm voxels, 21 keV
- Brighter spots are likely calcium hydroxide
- Technique could be useful for quantification in blended cement (portland-pozzolan) systems

Cement Hydration : Synchrotron Microtomography

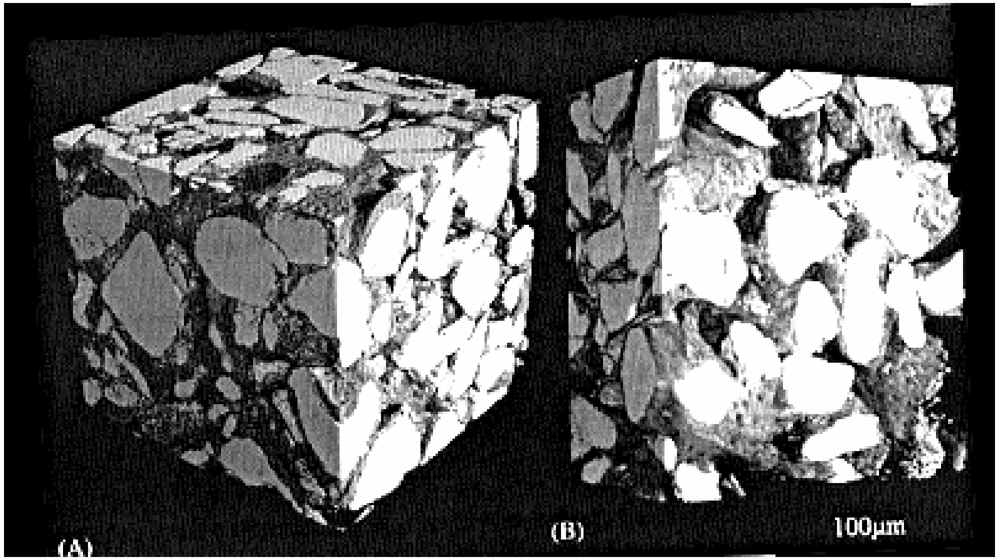
Introduction of toluene to cement paste results in large voids or vesicles in the hardened material, likely initially filled with the hazardous organic waste.



Butler, L.G., Owens, J.W., Cartledge, F.K., Kurtz, R.L., Byerly, G.R., Emery, E.F., Dowd, B, and Xie, X. (2000) *Env. Sci. Technol.*, 43:3269-75.

Cement Hydration: Synchrotron Microtomography

Very small(~1mm) samples of calcium phosphate (bone) cement on bone have been examined by phase-contrast microtomography.



Chotard, T.J., Smith, A., Boncoeur, M.P., Fargeot, D. and Gault, C. (2003) *J. Eur. Cer. Soc.*, 23:2211-23.

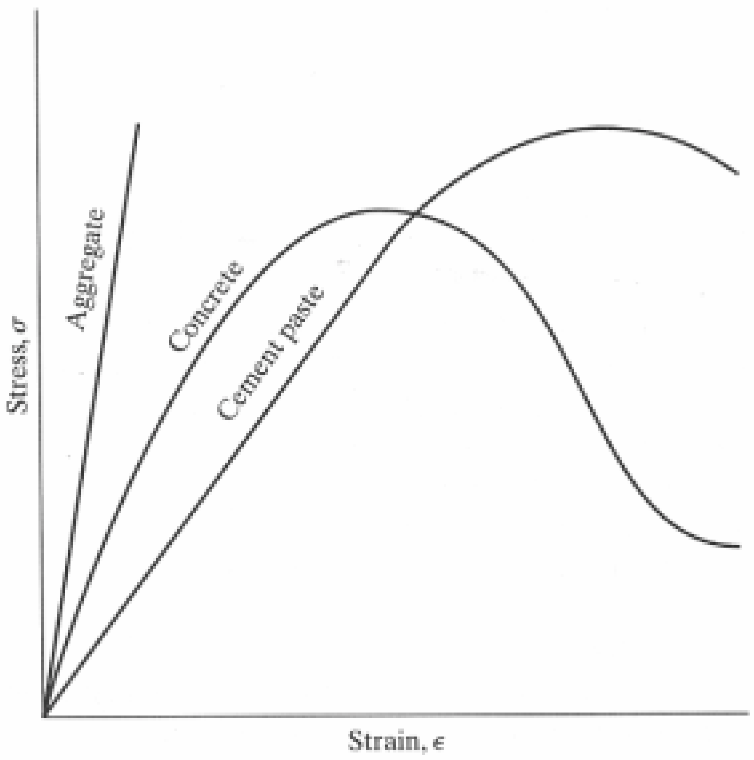
Cement Hydration

Research opportunities exist in:

- Nanoscale characterization (structure and composition) of C-S-H
- Coupled imaging and phase identification (diffraction?) in simplified and complex systems at realistic water-to-cement ratios
- Characterization of cement hydration at low and high temperatures and at high temperature and pressure (oil well applications)
- Time-resolved characterization (imaging and quantification) of the effects of chemical admixtures and “green” supplementary cementing materials on reaction kinetics, chemistry, and structure

Loading

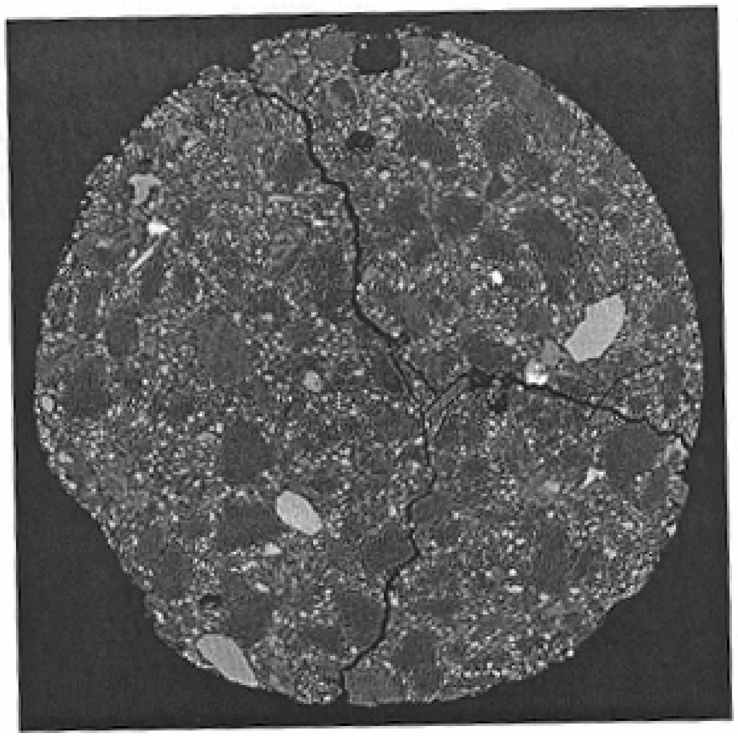
- Establishing true structure-property relationships has been challenging because of the multi-scale heterogeneity of cement-based materials
- Concrete is considered to be a 3 phase material: paste or mortar fraction + coarse aggregate + agg/paste interface

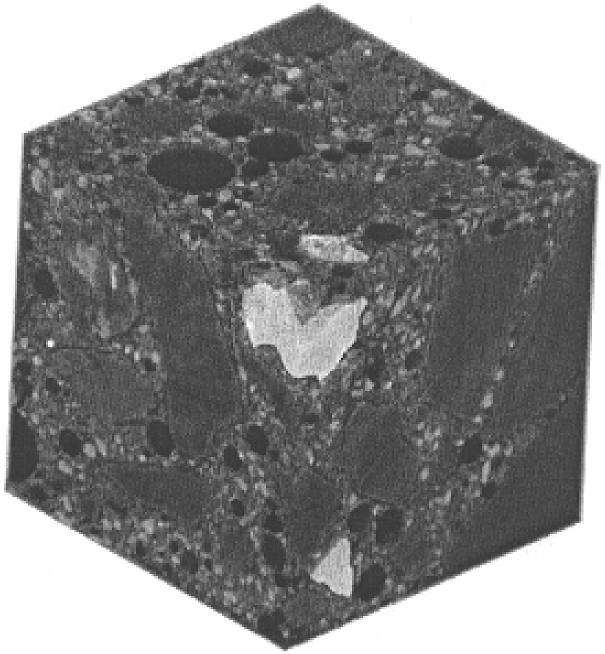


10-50μm

Loading: Synchrotron Microtomography

- Microtomography at BL X2B (NSLS) was used to examine internal cracking in 4x8 mm cylindrical mortar samples under compression
- Data describing the three-dimensional crack surfaces generated was related to fracture energy, by dW/dA = d(F-U-C)/dA





Landis, E.N., Nagy, E., and Keane, D.T. (2003) *Eng. Fracture Mech.*, 70:911-25.

Loading

Synchrotron-based research opportunities exist in:

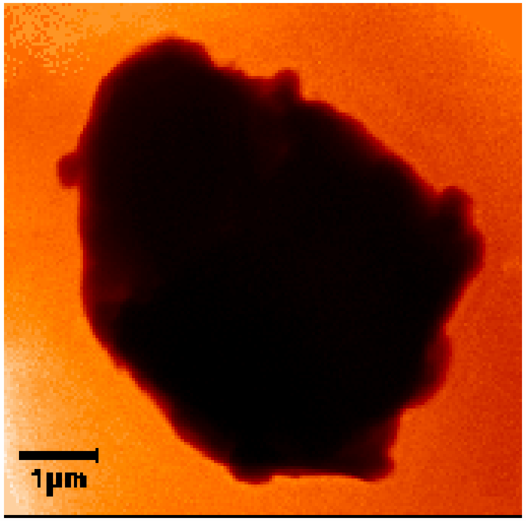
- Fracture in ultrahigh performance “concretes”
- Strength, stiffness measurements of individual components, for modeling complex materials
- Creep in cement paste
- Damage propagation due to combinations of loading and environment

Durability

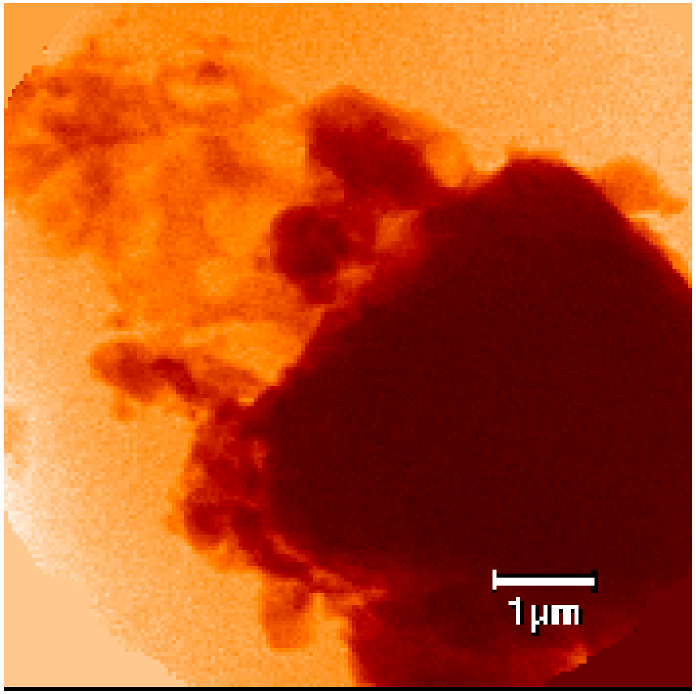
- Sulfate attack, including thaumasite formation
- Alkali-silica reaction
- Delayed ettringite formation
- Leaching
- Acid attack
- Carbonation
- Abrasion
- Erosion
- Freeze/thaw
- Fire
- Corrosion of reinforcing steel

Durability: TXRM

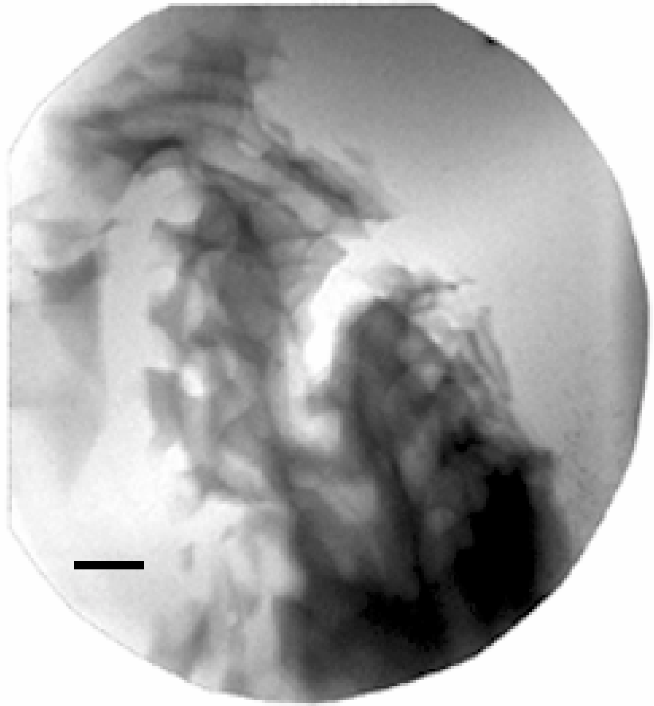
Alkali-Silica Reaction



"Dry" ASR gel;
Not in solution



ASR gel in 0.05M NaOH at pessimum proportion



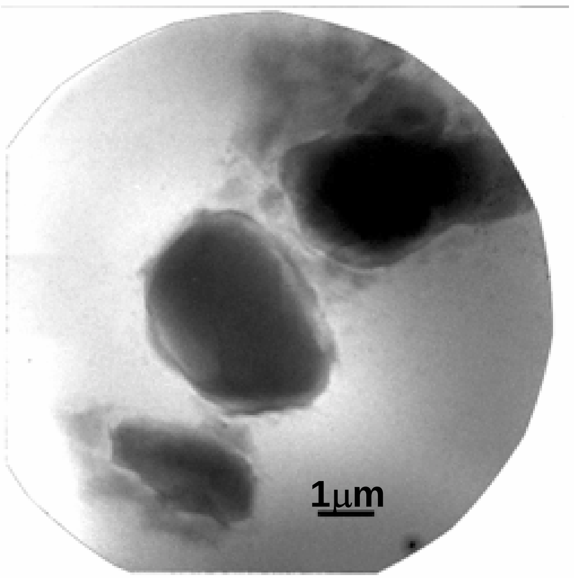
ASR gel in 0.7M NaOH at pessimum proportion

K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, and W. Meyer-Ilse, *Journal of Microscopy*, December 1999, V196: 288-298.

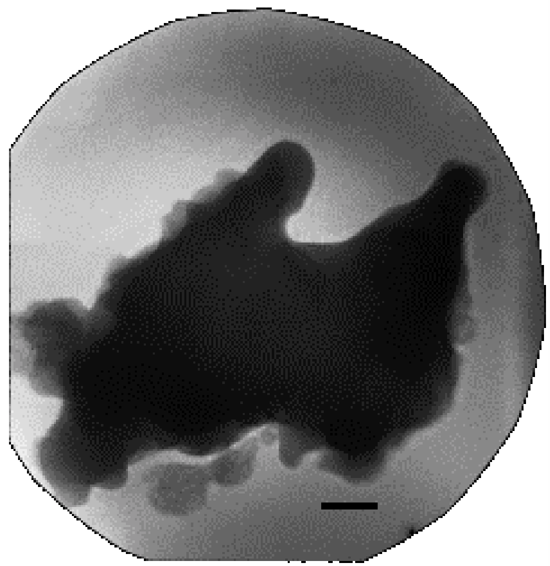
K.E. Kurtis, P.J.M. Monteiro, J.T. Brown, and W. Meyer-Ilse, *Cement and Concrete Research*, March 1998, V28:411-421.

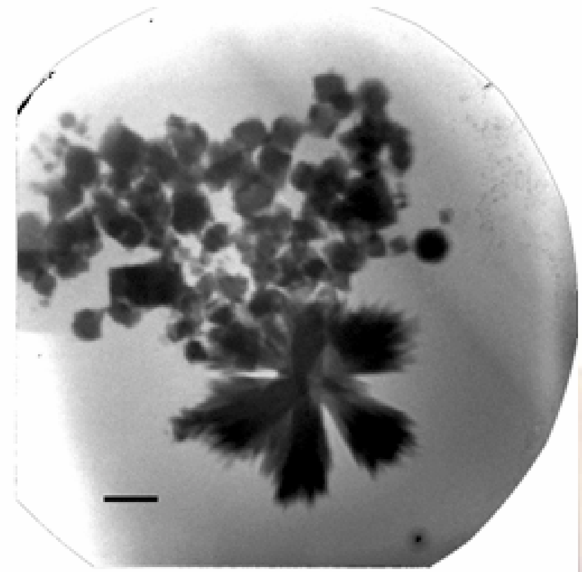
Durability: TXRM

Examination of the effect of chemical additives to control expansion by alkali-silica reaction



After 1 week in 0.7M NaOH + 10% acetone



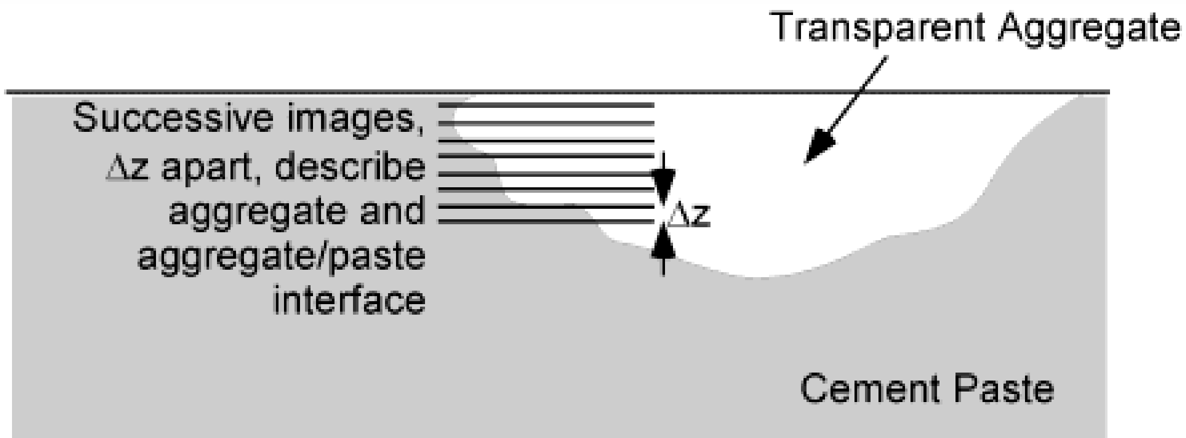


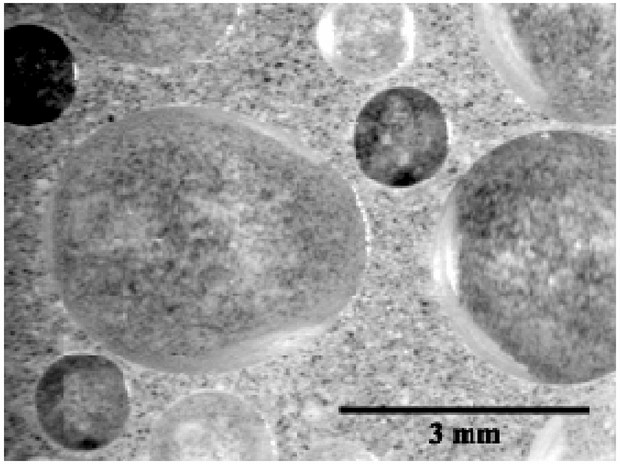
After 1 week in 0.7M NaOH + 0.1M LiCl

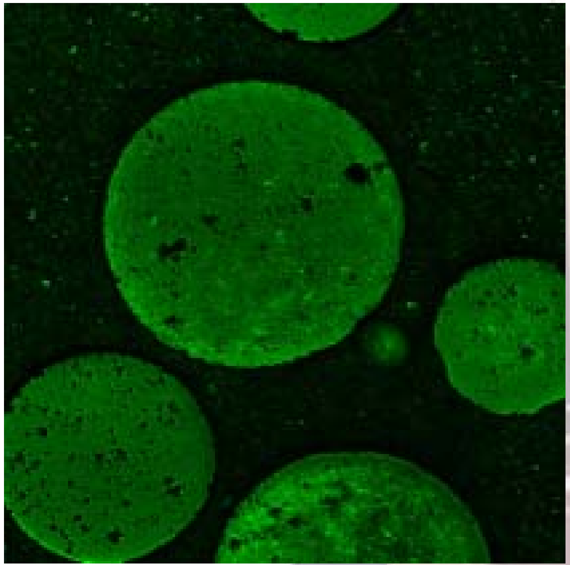
K.E. Kurtis and P.J.M. Monteiro, *Journal of Materials Science*, May 2003, V.38, n. 9: 2027-36.

Durability: Confocal X-ray Imaging

- Optical sectioning is limited to transparent materials





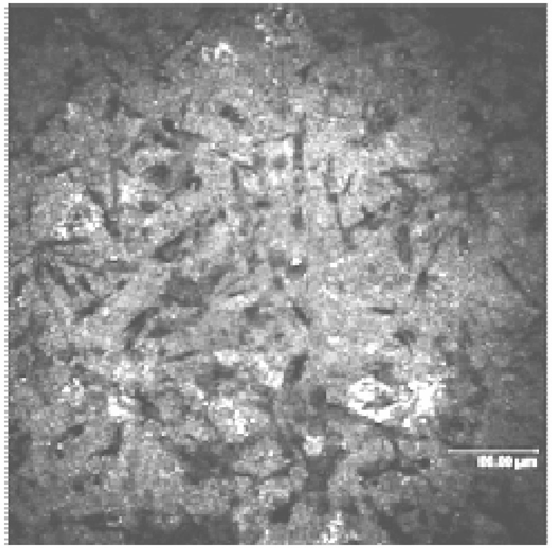


K.E. Kurtis, N.H. El-Ashkar, C.L. Collins, and N.N. Naik, *Cement & Concrete Composites*, October 2003, V.25(7):695-701.

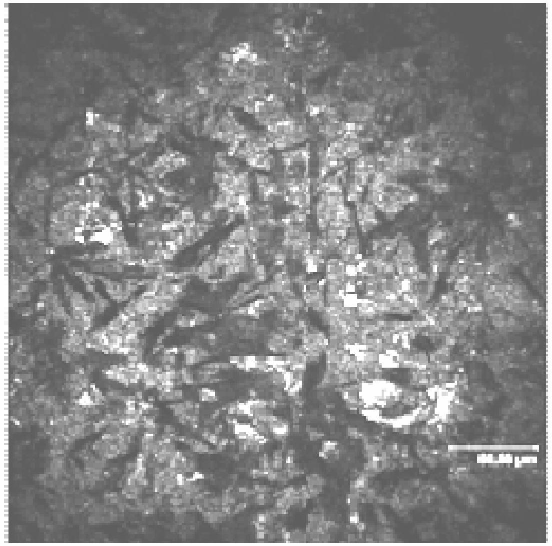
C.L. Collins, J.H. Ideker, and K.E. Kurtis, *Journal of Microscopy*, Feb 2004, V.213(2):149-157.

This material is based upon work supported by the National Science Foundation under CMS-0074874. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of NSF.

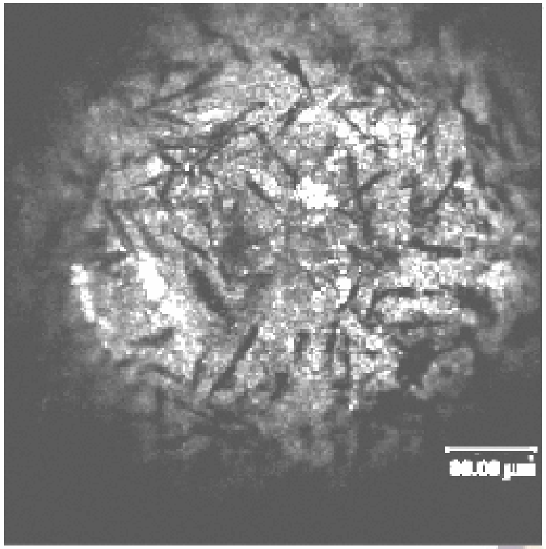
Durability: Confocal X-ray Imaging



$LiNO_3$, Li/Na=1.0, 3 days



$LiNO_3$, Li/Na=1.0, 8 days



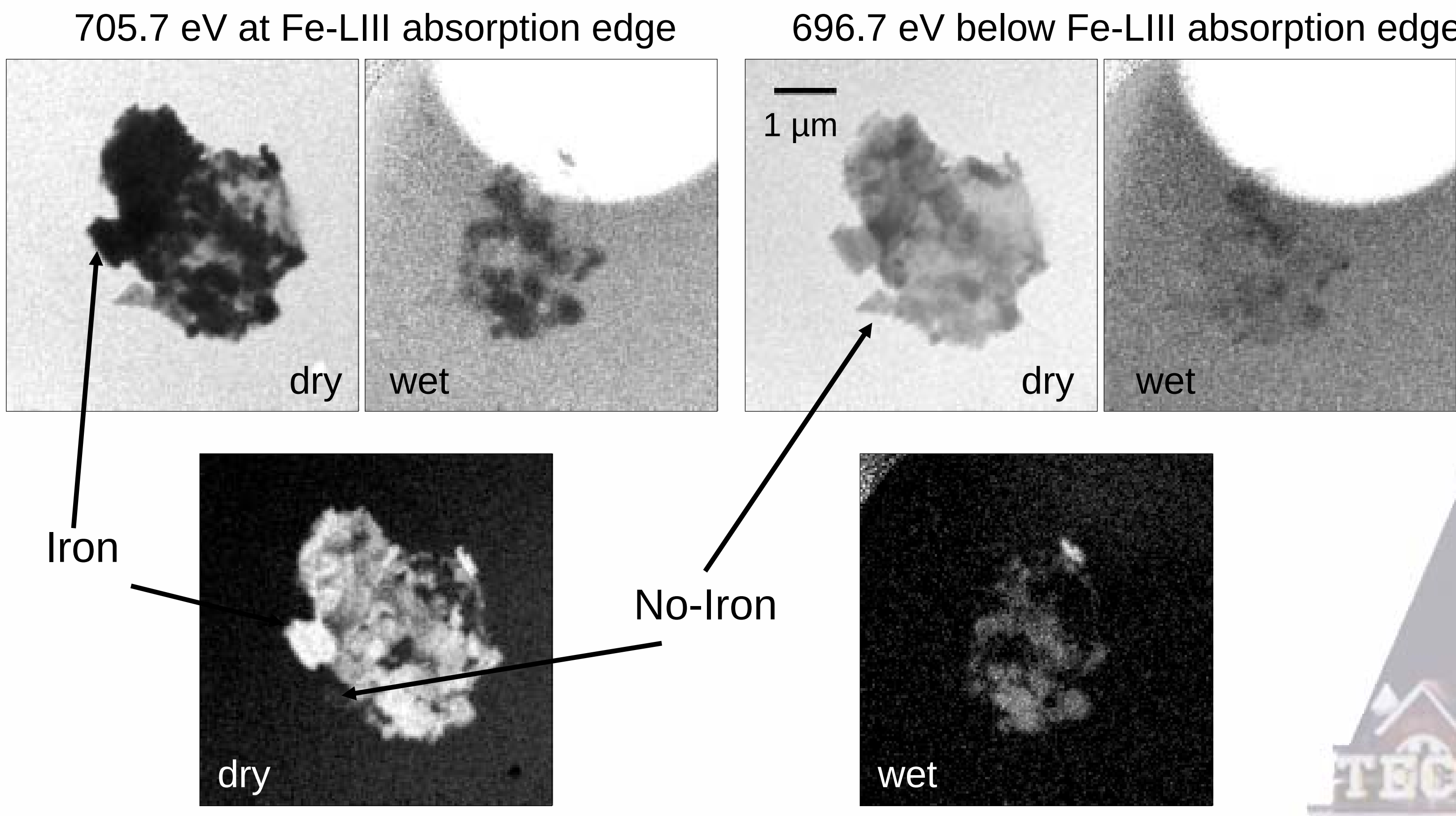
LiOH, Li/Na=0.50, 1 day

- Lathlike reaction products apparent at the aggregate/cement interface in the presence of lithium only.
- Technique could also by used for characterization of cement hydration products formed via bottle hydration and at aggregate/paste interfaces

C.L. Collins, J.H. Ideker, G.S. Willis, and K.E. Kurtis, *Cement and Concrete Research*, in press.

Durability: TXRM

- *In situ* study of corrosion of steel filings

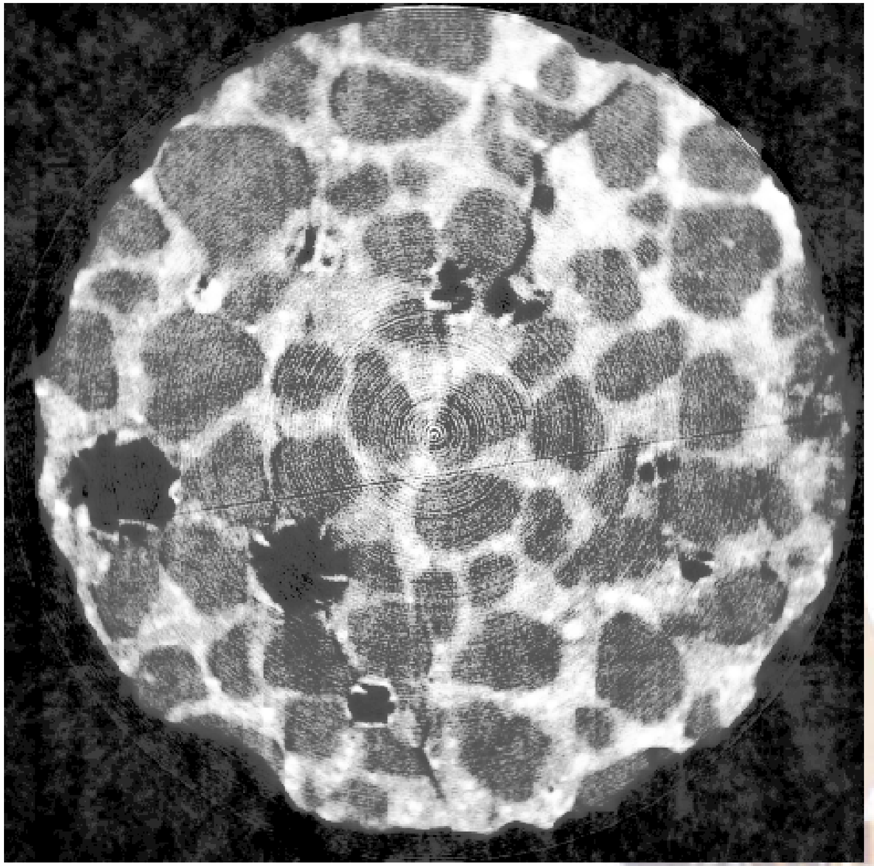


Iron Distribution (mass/area)

Kurtis, K.E., Meyer-Ilse, W., and Monteiro, P.J.M., *Corr. Sci.* 42:1327-36.

Durability: Synchrotron Microtomography

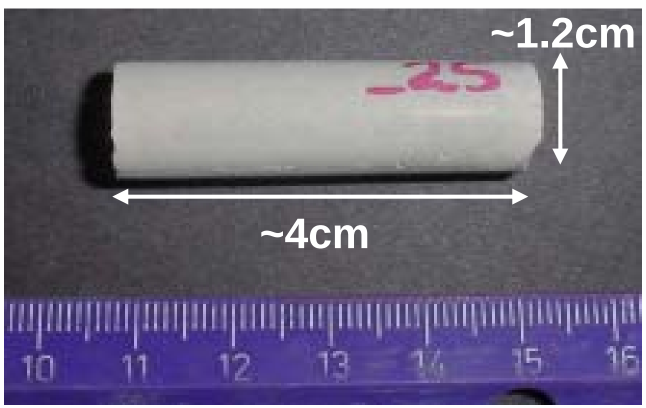
- The first synchrotron imaging of cement-based material found in the literature reports sulfate damage to an epoxy-impregnated 3.5mm-diameter sample cored from a standard mortar bar, as examined by Bentz and co-workers (1995) at BL X-2B at NSLS

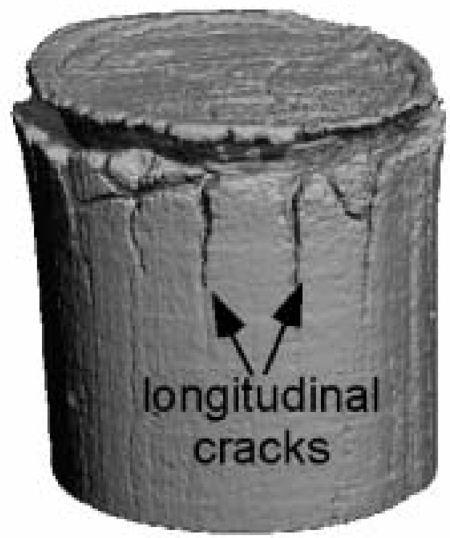


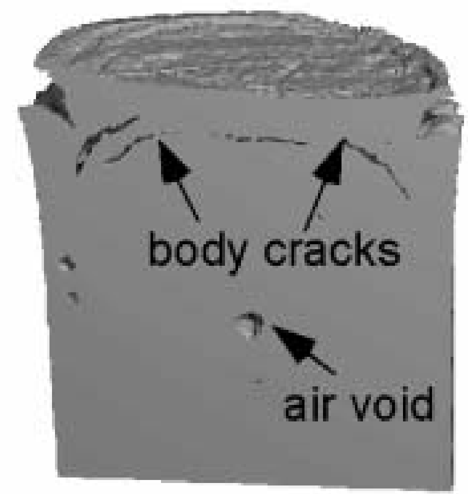
Bentz, D.P., Martys, N.S., Stutzman, P., Levenson, M.S., Garboczi, E.J., Dunsmuir, J., and Schwartz, L.M. (1995) *Proc.Microstructure of Cement-based Systems: Bonding and Interfaces in Materials*, Diamond, S., Mindess, S, Glasser, P., Roberts, L.W., Skalny, J.P., and Wakeley, LD. (Eds.), Materials Research Society.

Durability: Lab-based microtomography with EDXRD

- 70 kVp x-ray tube
- Detector with 2048 x 64 elements and 24μm pitch
- After identifying the top of the sample via scout view, 390 slices were imaged 50μm apart (4.5 hours/sample)





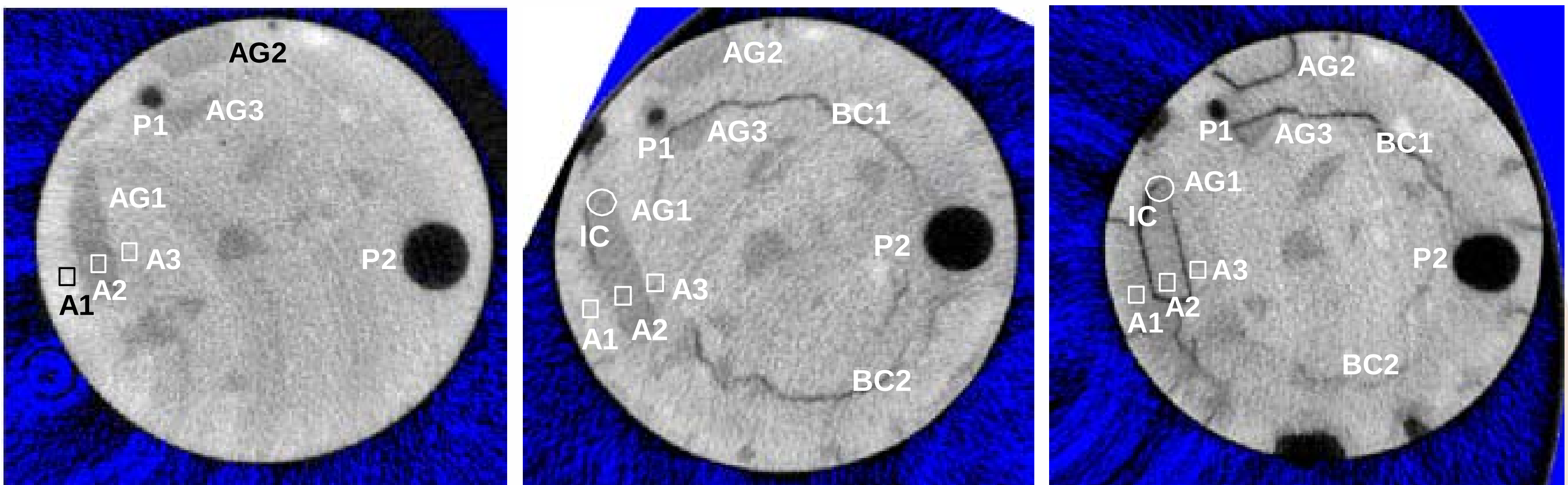


S.R. Stock, N.N. Naik, A.P. Wilkinson, and K.E. Kurtis, *Cement and Concrete Research*, October 2002, V.32:1673-5.
N.N Naik, A.C. Jupe, S.R. Stock, A.P. Wilkinson, and K.E. Kurtis, *Cement and Concrete Research*, in review.

This material is based upon work supported by the National Science Foundation under CMS-008482. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of NSF.

Durability: Lab-based microtomography with EDXRD

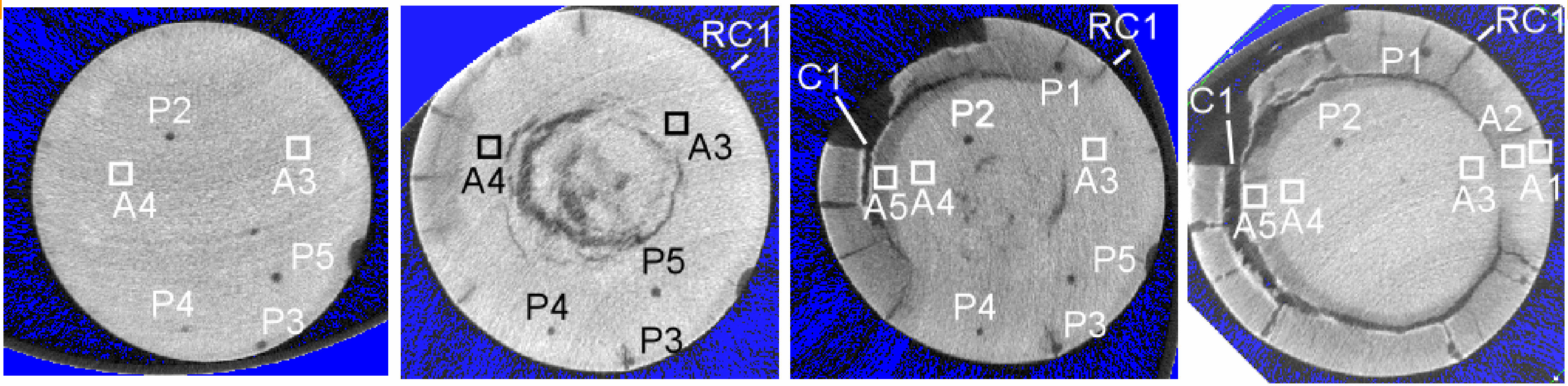
- Type I cement paste-aggregate sample at w/c = 0.485 and exposed to 10,000 ppm of sulfate ions in sodium sulfate solution



7 weeks | 17 weeks | 29 weeks

S.R. Stock, N.N. Naik, A.P. Wilkinson, and K.E. Kurtis, *Cement and Concrete Research*, October 2002, V.32:1673-5.
N.N Naik, A.C. Jupe, S.R. Stock, A.P. Wilkinson, and K.E. Kurtis, *Cement and Concrete Research*, in review.

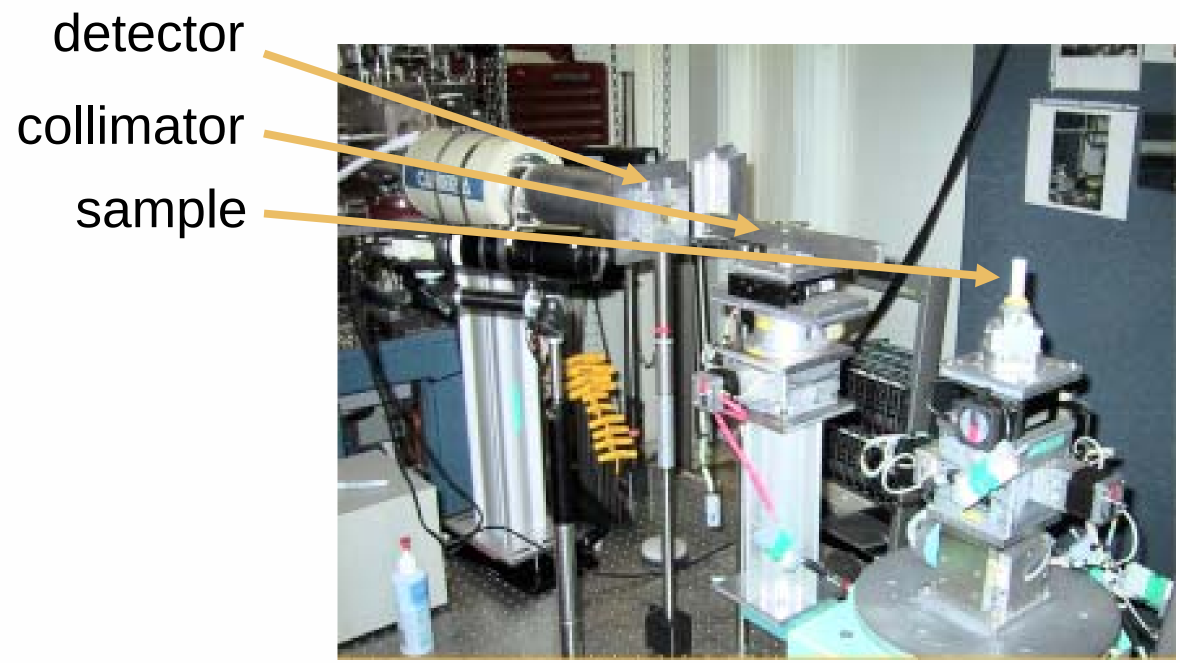
Durability: Lab-based microtomography with EDXRD



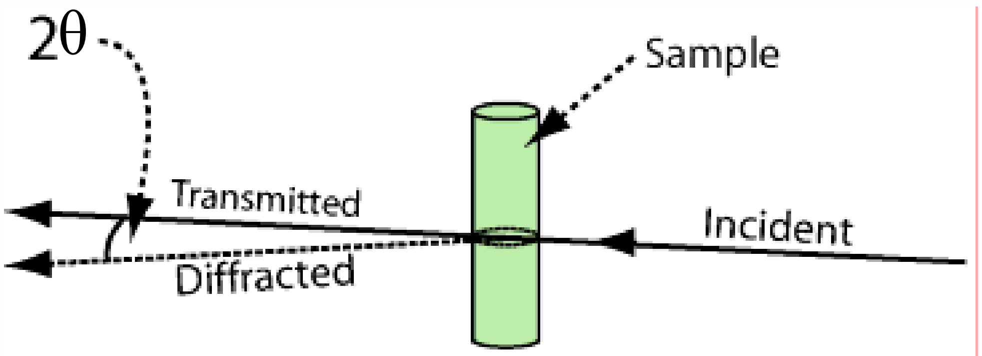
	Linear attenuation coefficient, μ cm^{-1})							
Time	**21 weeks**		**36 weeks**		**42 weeks**		**52 weeks**	
	Av μ	**Std. dev.**	**Av μ**	**Std. dev.**	**Av μ**	**Std. dev.**	**Av μ**	**Std. dev.**
A1	-		-		-		2.0	0.1
A2	-		-		-		1.7	0.2
A3	2.2	0.1	2.0	0.1	2.2	0.1	2.0	0.1
A4	2.3	0.2	2.0	0.1	2.0	0.1	2.0	0.2
A5	-		-		1.3	0.1	1.5	0.1

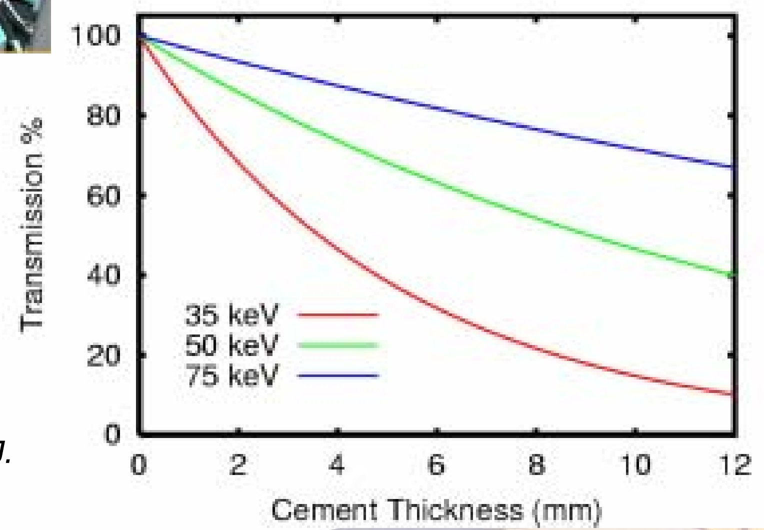
- A less dense region with darker color is observed near crack C1.
- The less dense region adjoining the crack (A5) is proposed to be due to leaching of calcium hydroxide, decalcification of C-S-H, or some other dissolution process resulting from exposure to the external solution at the cracked surfaces.

Durability: Lab-based microtomography with EDXRD



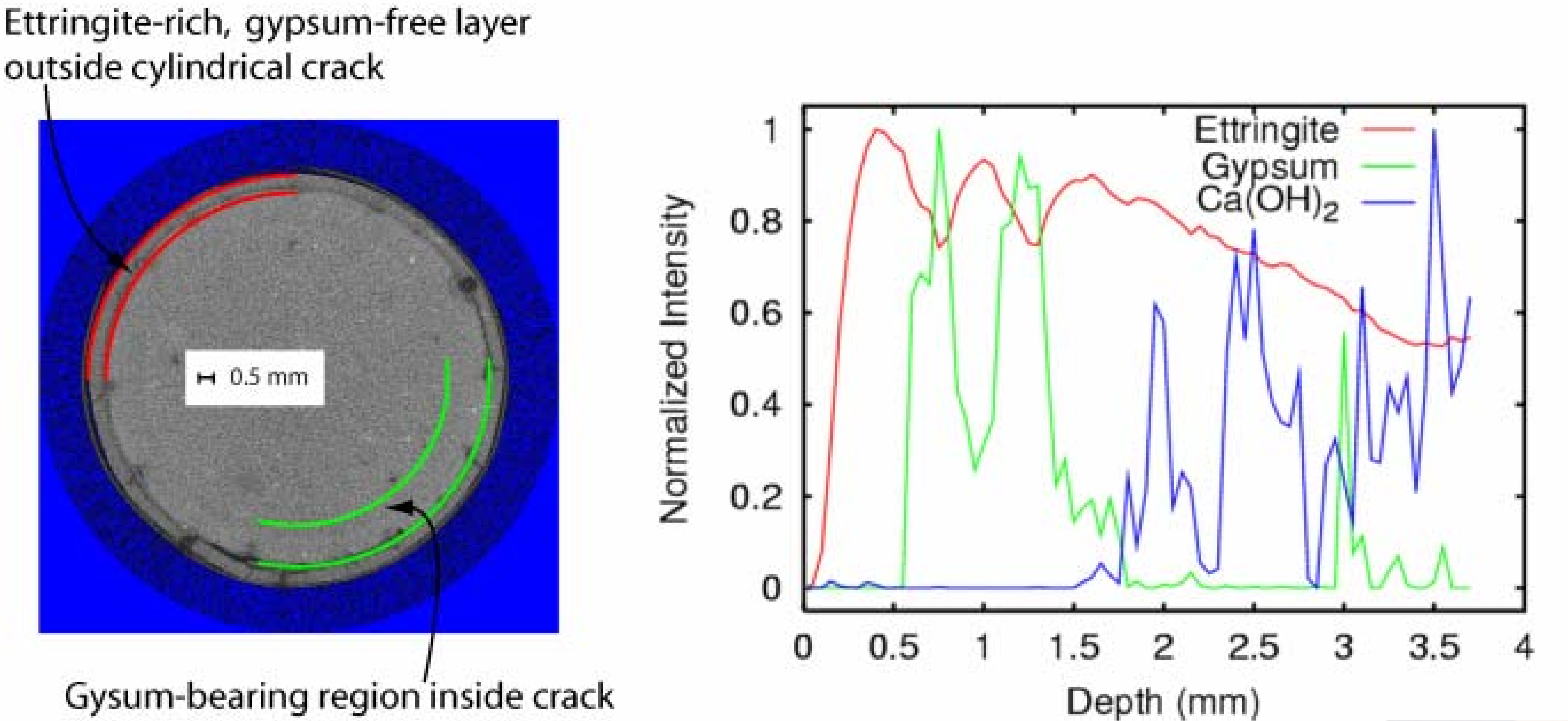
- EDXRD performed at XOR's 1 ID at APS





A.C. Jupe, S.R. Stock, P.L. Lee, N. Naik, K.E. Kurtis, and A.P. Wilkinson, *J. Applied Crystallography*, accepted for publication.

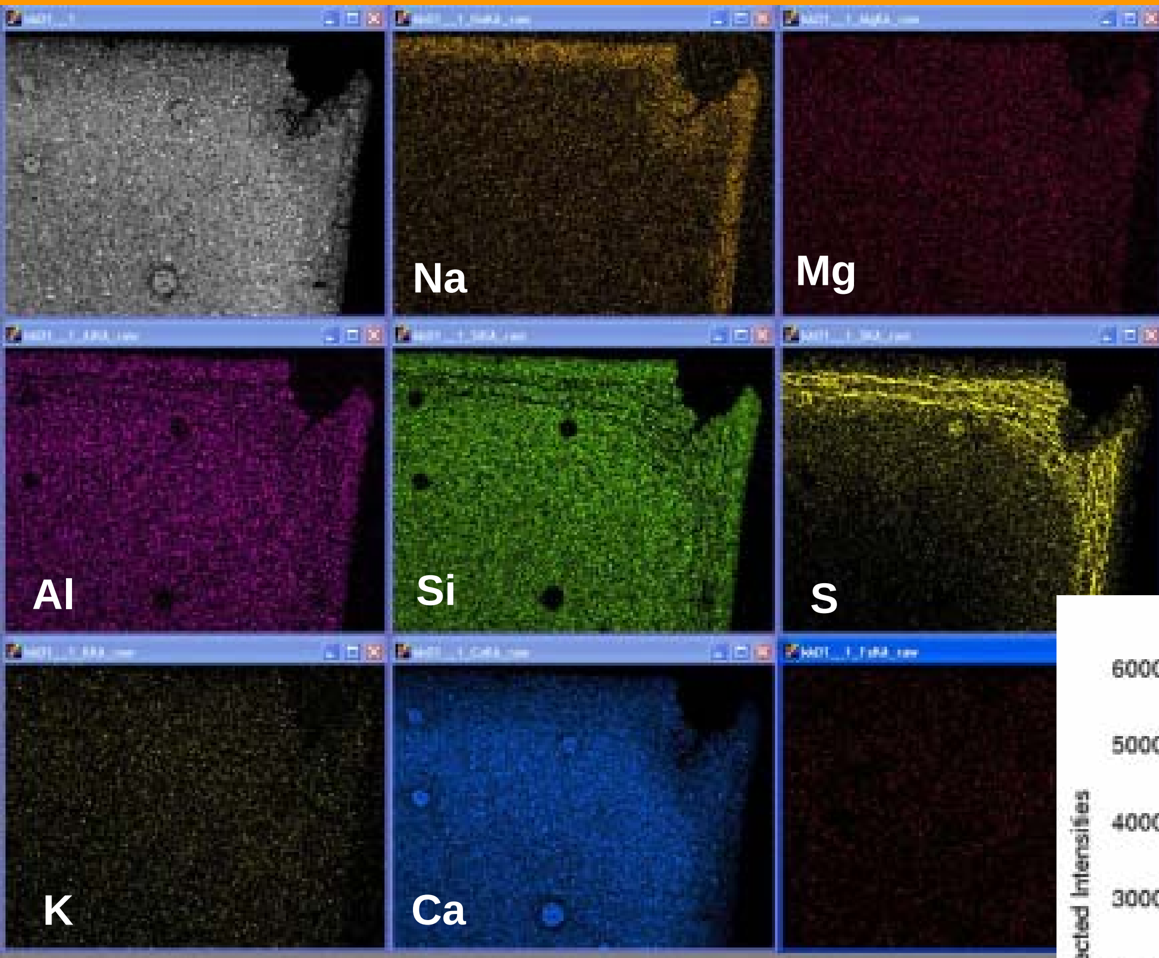
Durability: Lab microtomography with EDXRD



N.N. Naik, A.C. Jupe, S.R. Stock, A.P. Wilkinson, and K.E. Kurtis, "submitted to *Cement and Concrete Research*.

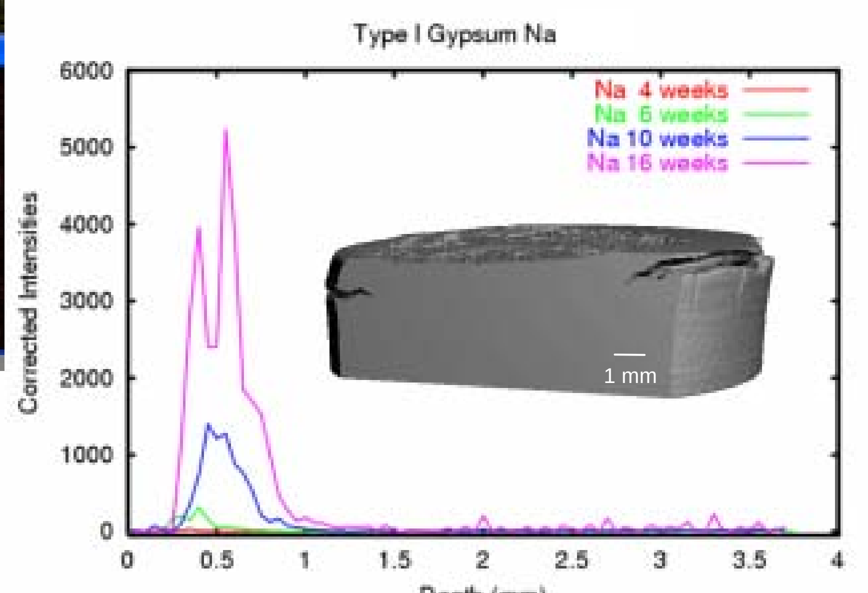
A.P. Wilkinson, C. Lind, S.R. Stock, K.E. Kurtis, N. Naik, D.R. Haeffner, and P.L. Lee, *Materials Research Society Symposium Proceedings Series*, V. 678, EE5.3.1, San Francisco, CA, April 14-20, 2001.

Durability: Lab microtomography with EDXRD *and SEM*



Field of view = 4mm

- Spatial relationship between structure and chemistry is key to understanding underlying damage process



Durability

Some opportunities for further synchrotron-based research:

- *In situ* imaging for damage process monitoring

  - imaging at variable temperature, RH
- Combined imaging and chemical/phase analysis

  - adequate resolution to capture changes in small capillary pores (5-50 nm) and to detect microcracks
- Post-imaging *quantitative analysis* to measure crack surface area, pore connectivity, etc., which can then be used to link composition and performance
- Simply too many high-value potential applications to list here…

Concluding Remarks

X-ray imaging affords some clear benefits for the characterization of cement-based materials, including

- Non-destructive examination and/or sectioning of opaque cement-based materials
- High resolution
- Rapid data acquisition
- Characterization of hydrated samples at normal temperature and pressure, if desired.

Concluding Remarks

Developments which would be beneficial for researchers in the cement-based materials community include:

- Coupling of imaging and diffraction or elemental analysis
- Sample indexing systems which function *between* beamlines
- Dedicated beamlines for imaging, avoiding complicated and time-consuming set up and break down
- User support for imaging, reconstruction, and analysis
- Ability to image larger samples, even at lower resolution
- On-site microscopy/tomography facilities for sample pre-view, to locate regions of interest
- Imaging at resolution < 50nm